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Synthesis and characterization of cellulose acetate from rice husk: Eco-friendly condition

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ABSTRACT

Cellulose acetate was synthesized from rice husk by using a simple, efficient, cost-effective and solvent-free method. Cellulose was isolated from rice husk (RH) using standard pretreatment method with dilute alkaline and acid solutions and bleaching with 2% H_2O_2. Cellulose acetate (CA) was synthesized successfully with the yield of 66% in presence of acetic anhydride and iodine as a catalyst in eco-friendly solvent-free conditions. The reaction parameters were standardized at 80 °C for 300 min and the optimum results were taken for further study. The extent of acetylation was evaluated from % yield and the degree of substitution (DS), which was determined by ^{1}H NMR and titrimetrically. The synthesized products were characterized with the help modern analytical techniques like FT-IR, ^{1}H NMR, XRD, etc. and the thermal behavior was evaluated by TGA and DSC thermograms.

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1. Introduction

Lignocellulosic biomass is the most abundant renewable biomass on the earth with a worldwide yearly supply of approximately 200 billion tones (Ragauskas et al., 2006; Sánchez & Cardona, 2008; Zhang, 2008). Lignocellulosic biomass comprising forestry, agricultural and agro-industrial wastes are inexpensive, relatively carbon-neutral source of energy sources (McKendry, 2002). An intense research scrutiny was currently undertaken worldwide to identify attractive chemical transformations to convert biomass into organic chemicals and to develop economically feasible processes for these transformations on a commercial scale (Naik, Goud, Rout, & Dalai, 2010). Lignocellulosic biomass is composed of cellulose, hemicelluloses and lignin as well as other minor components. Among them cellulose is the most abundant renewable organic material produced in the biosphere and widely distributed in higher plants, in several marine animals, and to a lesser degree in algae, fungi, bacteria, invertebrates, and even amoeba (Habibi, Lucia, & Rojas, 2010). Cellulose is a polysaccharide made of D-glucose connected together via β-1,4-glycosidic bonds and is a promising raw material for producing important chemicals, including cellulosic-ethanol, hydrocarbons, and starting materials for the production of polymers (Hahn-Häegerdal, Galbe, Gorwa-Grauslund, Lidén, & Zacchi, 2006; Mosier, Sarikaya, Ladisch, & Ladisch, 2001; Ragauskas et al., 2006).

The production of cellulose derivatives has extensive interest worldwide, mainly because of its abundance in nature, its biodegradability and its lower environmental impact in comparison with polymers obtained from fossil sources (Zhang, 2007). Nowadays derivatives of cellulose have been widely used in waste treatment, oil recovery, paper manufacturing, textile finishing, food additives and pharmaceutical application (Yan, Li, Qi, & Liu, 2006). Cellulose acetate, one of the important derivatives of cellulose which are industrially more important and it is estimated that annually 1.5 billion pounds are manufactured globally (Biswas, Shogren, & Willett, 2005). Cellulose acetate has vast industrial applications such as coatings, cigarette filters, textile fibers, consumer products, filtration membranes, composites, laminates, and medical and pharmaceutical products (Yu et al., 2013; Li et al., 2009; Yu, Yu, Chen, Williams, & Wang, 2012).

Traditionally, cellulose acetate is produced from native cellulose like sugarcane bagasse by Cerqueira and his co-workers, polysaccharide by Edgar and his co-workers and valonia cell by Sassi and his co-workers using acetic acid and acetic anhydride in the presence of a sulfuric acid as a catalyst (Cerqueira, Filho, & Meireles, 2007; Edgar et al., 2001; Sassi & Chanzy, 1995). But in the recent time, synthesis of cellulose acetate includes the use of ionic liquids in room temperature using any catalyst (Wu et al., 2004), superacids like $SO_4{}^{2-}/ZrO_2$ in a solvent free ball milling reactor (Yan et al., 2006), dialkylcarbodiimide, N,N-carbonyldiimidazole, iminium chlorides (Heinze, Liebert, & Koschella, 2006) and iodine as a catalyst for

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esterification of cellulose and corn starch (Biswas et al., 2005) cellulose and starch (Biswas et al., 2007) and polysaccharide (Biswas et al., 2009) in the presence of acetic anhydride. The catalysts used by the researchers were eco-friendly and have no pollution effect to the environment. Only sulfuric acid has some effect to the environment, so researchers tried to solve the problem and have great success with high yield of the product, cellulose acetate.

The present paper focused on the preparation of cellulose acetate in heterogeneous medium using iodine as catalyst. Being as cheap, convenient, commercially available and environment friendly reagent, iodine is currently being extensively explored regarding its catalytic properties on various substrates in various organic synthesis (Behmadi, Roshani, & Saadati, 2009; Biswas, Saha, Lawton, Shogren, & Willett, 2006; Phukan, 2004; Yadav, Reddy, Rao, & Reddy, 2003; Yadav et al., 2008). So, we have selected the catalyst as iodine in presence of acetic anhydride and also till this time no work had been reported on preparation of cellulose acetate from rice husk using eco-friendly solvent free condition with good yield 66%.

2. Materials and methods

2.1. Materials and chemicals

Rice Husk used in the experiments was supplied by local rice milling industry, Bhatemora Rice Mill Pvt. Ltd., Jorhat, Assam (North-East part of Assam). RH was extensively washed with distilled water in order to remove impurities (mainly dust). The materials were first dried in sunlight and cut into smaller pieces and milled to pass through a 1–2 mm mesh. The milled samples were then stored at room temperature. The reagents and chemicals using in our study were of standard analytical grades such as acetic anhydride, iodine, sodium thiosulfate, ethanol, sodium hydroxide, hydrochloric acid, methylene chloride and other chemicals. All reagents were used without further purification.

2.2. Isolation of cellulose from rice husk

Dry powdered RH sample was extracted with mixture of organic solvent (hexane–methanol) (2:1, v/v) using Soxhlet apparatus for 10 h for removal of the oil/wax etc. After that the delignification was undergoing follow-up with two-step processes. At first the extractive free rice husk (10 g) was soaked in 300 ml different types of alkali (5%, w/v) with ratio of liquor to material 30:1 and heated to 80 °C for 5 h. After alkali treatment, slurry was allowed to cool and treated with 10% H_2SO_4 acid to neutralize the solution with 3–4 of pH value at 50 °C. After that the biomass was separated by filtration through Buchner funnel using vacuum pump. The residual biomass was then undertaking for bleaching treatment using 2% H_2O_2 solution with pH value 9 and ratio of liquor to material 30:1 and stirring for 5 h at room temperature. The chemical modification of lignocellulosic biomass was achieved by using oxidizing agents, such as H_2O_2 to improve their properties and make them suitable for different uses (Salam, Reddy, & Yang, 2007; Wójciak et al., 2007). After bleaching, the biomass was washed with distilled water for several times. After filtration samples were oven dried (Fig. 1) and the content of alpha-cellulose was then determined according to TAPPI standard method T203 (Amal, Moustafa, Khodair, & Hammouda, 2007; Guozhi et al., 2013).

2.3. Acetylation of cellulose

For the preparation of cellulose acetate, 0.2 g of RH cellulose was taken in to a 100 ml round bottomed flask fitted with a mechanical stirrer. 10 ml acetic anhydride was added in to the material
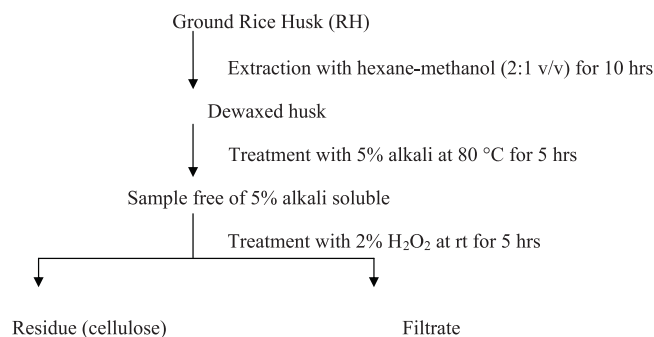

Ground Rice Husk (RH)

↓ Extraction with hexane-methanol (2:1 v/v) for 10 hrs

Dewaxed husk

↓ Treatment with 5% alkali at 80 °C for 5 hrs

Sample free of 5% alkali soluble

↓ Treatment with 2% H_2O_2 at rt for 5 hrs

Residue (cellulose)   Filtrate

Fig. 1. Flowchart for extraction of cellulose from RH.

and required amount of iodine was added for different concentrations (0.1, 0.15, 0.2, 0.25 and 0.3 g) accordingly. The mixture was heated to 50, 60, 70, 80, 90 and 100 °C and left for 60, 120, 180, 240, 300 min at 80 °C. At the end of every experiment, the reaction mixture was allowed to cool at room temperature and treated with 5 ml saturated solution of sodium thiosulphate with stirring. The colour of the mixture was changed from dark brown to colorless, indicating the transformation of iodine to iodide. The mixture was then transferred to a beaker containing ethanol (30 ml), stirred for 60 min. The product was filtered and thoroughly washed with 75% (v/v) ethanol and distilled water to remove the unreacted acetic acid and byproducts. The solid material was then dried at 60 °C in an oven. The oven-dry materials was dissolved in methylene chloride and filtered. Cellulose acetate was formed as a film in-side the flask after evaporating the filtrate. Ethanol was used to remove the film from the flask and filtered through a filter paper. The cellulose acetate collected on the filter paper was dried at 60 °C in oven for 24 h.

2.4. Determination of degree of substitution (DS)

The average value of acetate groups ($-CH_3COO$) groups that replace hydroxyls in every glucose cycle gives the degree of substitution (DS) (Cai et al., 2013) and the values were determined by ^1H NMR spectroscopy and by titration with aqueous sodium hydroxide solution (Mullen & Pacsu, 1942).

2.5. Characterization of the acetylated cellulose

The functional group and chemical structure were evaluated by FT-IR spectroscopy using a Perkin–Elmer FT-IR-2000 spectrometer. Thirty-two scans were accumulated for each spectrum at a resolution of $4 cm^{-1}$ in the region from 4000 to $400 cm^{-1}$, using KBr pellets. NMR spectra were recorded on Advance DPX 300 MHz FT-NMR spectrometer using tetramethylsilane (TMS) as an internal standard. Thermogravimetic analysis was performed with Universal V4.7A equipment from TA-Instrument at a heating rate of 10 °C/min from 30 °C to 600 °C under argon atmosphere. Powder X-ray (XRD) measurement was performed on a Rigaku Ultima IV diffractometer with Cu Kα radiation at 40 kV and 40 mA in the range of $2\theta = 5–60°$, and the scanning rate is 5°/min.

3. Results and discussion

3.1. Isolation of cellulose from RH

3.1.1. Pretreatment of RH

Alkali pretreatment was carried out to remove lignin and the hemicelluloses from RH. We have taking five different common alkalis and the mixture of alkali for our investigations. In the first step of alkaline pretreatment and acid treatment, solubilize the

Table 1
Removal of hemicellulose and lignin from rice husk.[a]

Sample No.	Alkali treatment			H_2O_2 treatment		Result		
	Alkali[b]	Concentration of alkali wt (%)	Acid[c]	Temperature (°C)	Time[d] (h)	Weight[e] (g)	Cellulose content wt (%)	Standard deviation[f] (±)
1	NaOH	5	H_2SO_4	80	5	6.5	65	1.26
2	NaOH + Na_2CO_3	5	H_2SO_4	80	5	7.6	76	1.7
3	$Ca(OH)_2$	5	H_2SO_4	80	5	6.9	69	1.8
4	KOH	5	H_2SO_4	80	5	6.0	60	2.16
5	Liquor NH_3	5	H_2SO_4	80	5	7.2	72	1.7

H_2O_2 (%, v/v) = 2.
Initial weight of the untreated rice husk = 10 g.

[a] The particle size of rice husk was in the range from 1 to 2 mm.
[b] Neutralize with 10% acid solution with 3–4 of pH value at 50 °C.
[c] Different types of alkali.
[d] Time of bleaching by H_2O_2.
[e] Weight (g) of the rice husk after treatment with alkali and H_2O_2.
[f] Calculated the standard deviation (±) for the cellulose content on triplicate data.

lignin and hemicellulose part and the second step was bleaching for whitening the RH after first step. The reaction parameters like time, temperature and acid etc. were studied for alkali pretreatment to evaluate the optimum reaction conditions and the results were shown in Table 1. The optimum conditions of the reactions were 5 h, 80 °C, H_2SO_4 and 5% NaOH + Na_2CO_3 for time, temperature, acid and alkali respectively. It was found that the reaction condition 2 i.e. 5 h, 80 °C, H_2SO_4 and 5% NaOH + Na_2CO_3 had best cellulose % compared with other four conditions with standard deviation ±1.7. Therefore the condition 2 was considered as optimal for our investigations.

Based on the results illustrated in Table 1, NaOH + Na_2CO_3 (5% aqueous solution) was taken as the solvent for isolating cellulose from rice husk and was shown by a flow chart (Fig. 1).

3.2. Optimization of the reaction conditions – temperature, time and catalyst (iodine)

The optimum condition for acetylation of RH cellulose was investigated in terms of reaction time and temperature using six different reaction temperatures and five different times respectively. The DS and yield (%) were calculated for each product and data was evident from Table 2. The rate of acetylation (%) increased progressively with increasing the reaction temperature from 50 °C up to 80 °C for 120 min and after that cellulose degradation and RH cellulose loses its original appearance. At reaction temperature 80 °C, the DS and yield (%) of cellulose acetate increased progressively with increasing the reaction time from 60 to 300 min. Long

reaction time allows acetic anhydride to react with cellulose thus substitute with the free hydroxyl group of cellulose. However at long reaction time degradation of cellulose and hydrolysis of cellulose acetate occurs (Hu, Chen, Xu, & Wang, 2011; Li et al., 2009), the condition of sample 16 was considered as optimal. Therefore the optimum condition for esterification reaction was 80 °C for 300 min.

Evidently the results indicate the important roles played by the reaction time and temperature. The yield (%) and DS increased as the reaction time and temperature increased. It was proposed that cellulose was acetylated heterogeneously at the beginning of the reaction. The solid cellulose is going through rapid surface acetylation and then as the acetylation progressed, the acetylated cellulose gradually dissolved in the reaction medium followed by subsequent acetylation of the remaining unreacted hydroxyl groups (Biswas et al., 2007). In addition, a significant increase in the swelling ability of cellulose and the diffusion rate of acetic anhydride and iodine was made by high temperature.

The effect of catalyst (iodine) concentrations was carried out using a series of different concentrations of iodine to study the effect on extent of acetylation (%). The DS and acetylation (%) increased gradually with increasing the iodine concentrations from 0.1 to 0.3 g. The data were given in Table 2 and the mechanism of the formation of cellulose acetate is outlined in Scheme 1 (Li et al., 2009). In the reaction process, iodine first activates the carbonyl carbon of acetic anhydride in the presence of alcoholic groups, as the oxygen of Cell-OH attacks the carbonyl carbon resulting in sp3

Table 2
Yield and degree of substitution (DS) of acetylated celluloses.

	Acetylation conditions	Acetylated cellulose				
A	Sample No.	1	2	3	4	5
	T (°C)[a]	50	60	70	80	90
	DS	0.85	0.93	1.01	1.08	–
	Yield (% dry weight)[c]	13	15	19	21	–
B	Sample No.	7	8	9	10	11
	T (min)[b]	60	120	180	240	300
	DS	0.95	1.08	1.25	1.84	2.12
	Yield (% dry weight)[c]	16	21	22	29	33
C	Sample No.	12	13	14	15	16
	Iodine (g)	0.1	0.15	0.2	0.25	0.3
	DS	2.58	2.63	2.8	2.85	2.91
	Yield (% dry weight)[c]	38	43	52	60	66

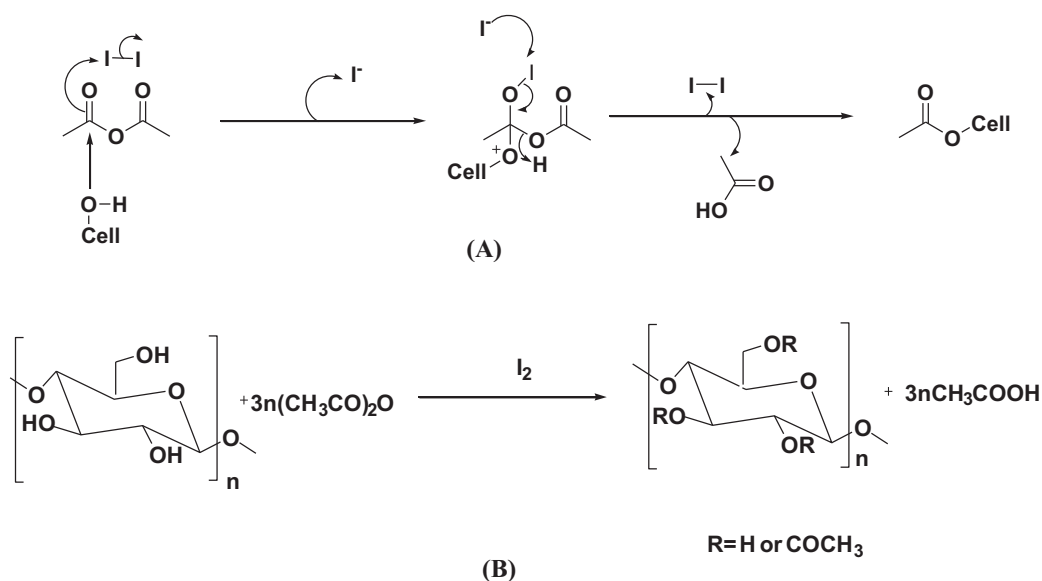A: t (min)[b] = 120; iodine (g) = 0.05.
B: T (°C) = 80; iodine (g) = 0.05.
C: T (°C) = 80; t (min) = 300.

[a] Reaction temperature.
[b] Reaction time.
[c] Increase weight of the sample (g).

Scheme 1. Mechanism of cellulose (cell-OH) acetylation using iodine as a catalyst represented by (A) and (B).

hybridization. The acetic anhydride reacts with hydroxyl groups involving a nucleophilic attack on the acyl carbon center of the acetic anhydride molecule by a lone pair of the alcoholic hydroxyl group followed by subsequent loss of acetic acid to generate the ester (Biswas et al., 2005; Hill, Jones, Strickland, & Centin, 1998). The addition of a saturated aqueous solution of sodium thiosulfate at the end of the reaction removes all the free iodine (Hussain et al., 2010).

As the data shown in Table 2, the DS and yield of the products increase with the increases of the quantities of iodine. This was resulted by the fact that in the condition of a great excess of acetic anhydride, more acetic anhydride-iodine intermediates have been produced while increasing the amounts of iodine, and thus cellulose was more easily acetylated (Biswas et al., 2009).

3.3. FT-IR

Characterization of the acetylated product was best examined by FT-IR spectroscopy. IR spectroscopic studies were performed using the KBr pellet technique to observe the ester peaks and hydroxyl group absorptions. Fig. 2 illustrates the FT-IR spectra of rice husk cellulose and acetylated product and Fig. 3 shows the IR spectra of different concentrations of the catalyst, iodine. The four major changes observed in the spectrum of acetylated RH cellulose as compared to the RH cellulose on acetylation are (i) a decrease in the hydroxyl ($-$OH) stretching band at $3322\,cm^{-1}$, (ii) an increase in the carbonyl (C=O) stretching band at $1751\,cm^{-1}$, (iii) an increase in the carbon–hydrogen (C–H) bending vibration at $1369\,cm^{-1}$, (iv) an increase in carbon–oxygen (C–O) stretching vibration at $1220\,cm^{-1}$ (Sun, Sun, & Sun, 2004).

The absorbance at 3322, 1632, 1384, 1192, 1122 and $753\,cm^{-1}$ are associated with native rice husk cellulose. The absorption band at $3990\,cm^{-1}$ is attributed to the $-$OH stretching vibration of rice husk cellulose. The band at $1632\,cm^{-1}$ is assigned to bending mode of the adsorbed water. The peak at $1384\,cm^{-1}$ corresponds to the $-$OH bending and that at $1192\,cm^{-1}$ related to the C–O anti-symmetric bridge stretching and all the contribution of the peaks are evidenced by literatures. In addition, the non-cellulosic polysaccharides were almost completely eliminated, as indicated by the absence of a peak at $1210\,cm^{-1}$ (Li et al., 2009). The spectrum (B) in Fig. 2 provides strong evidence of acetylation by showing the presence of three important ester bonds at 1751 (C=O ester), 1369 (C–H

bond in $-$OCOCH$_3$ group) and $-$CO$-$ stretching band of acetyl group at $1220\,cm^{-1}$ (Saikia, Ali, Goswami, & Ghosh, 1995). A strong band at $1051\,cm^{-1}$ is due to the C–O–C pyranose ring skeletal vibration. The disappearance of peaks in region $1840–1760\,cm^{-1}$ and at $1700\,cm^{-1}$ in spectrum (B) indicated that the product is free of the unreacted acetic anhydride and the by-product, acetic acid (Sun et al., 2004).

3.4. ^1H NMR

The ^1H NMR of prepared cellulose acetate recorded in CDCl$_3$ is shown in Fig. 4. All chemical shifts were given in parts per million (δ) downfield from tetramethylsilane as internal standard. The peaks at 1.9–2.2 ppm, corresponds to three methyl protons of acetyl groups and the peaks at 3.6–5.2 ppm corresponded to the seven anhydroglucose protons (Basta & Hosny, 1998; Heinze & Rahn, 1996; Mao & Ritcey, 1999). The degree of substitution was calculated by dividing 1/3 of the acetyl peak area by 1/7 of the anhydroglucose area.

3.5. Thermal analysis

The thermal properties of RH cellulose and acetylated cellulose products were examined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in the temperature range from 30 to 600 °C at a rate of 10 °C/min under argon flow. The results obtained from the typical TGA and DSC curves of the RH cellulose and acetylated cellulose sample 16 are shown in Fig. 5(a) and (b), respectively. As observed from Fig. 5, from room temperature to 120 °C the TGA curve of RH cellulose displayed a minor weight loss due to water desorption, which is not obvious for the acetylated products. This indicates that the acetylated products are more hydrophobic than the native cellulose. The crystalline region started to destruct and the polymer simultaneously decomposes from 225 to 400 °C, which evidently resulted in amorphous structure increases and the degree of polymerization decreases. During this stage from 400 to 550 °C, the crystalline region has been completely destructed and the cellulose decomposed into monomer of D-glucopyranose, which could be further decomposed into free radical (Antal & Varhegyi, 1995; Yang, Xu, Ma, & Wang, 2008). The onset thermal degradation temperatures were considered to start at 283 °C for native cellulose, 326 °C for acetylated product, and the
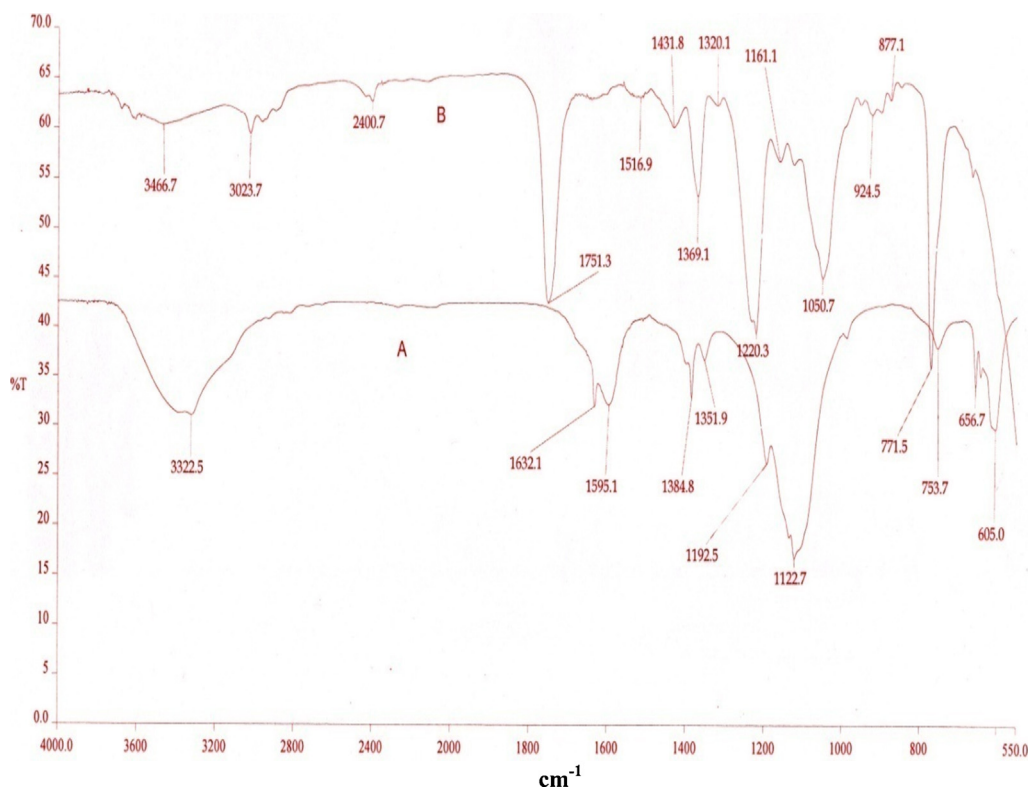
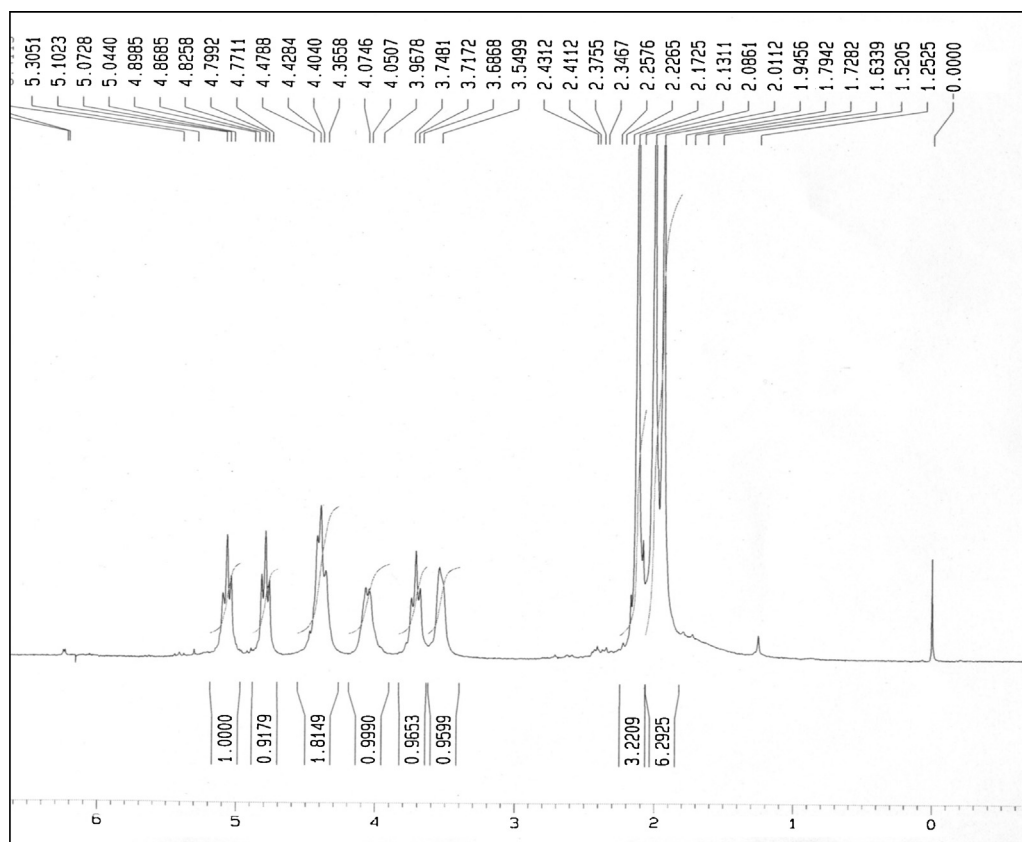**Fig. 2.** FT-IR spectra of (A) treated RH cellulose and (B) cellulose acetate.

Fig. 3. ^{1}H NMR spectrum of cellulose acetate in CDCl$_3$ prepared from rice husk cellulose.
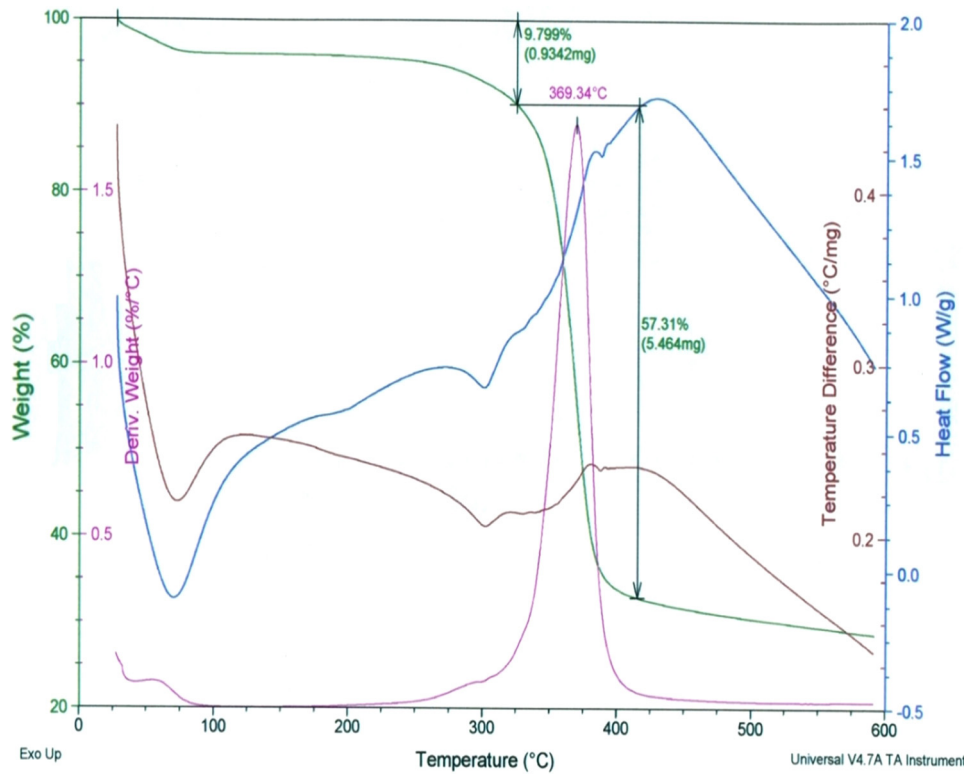
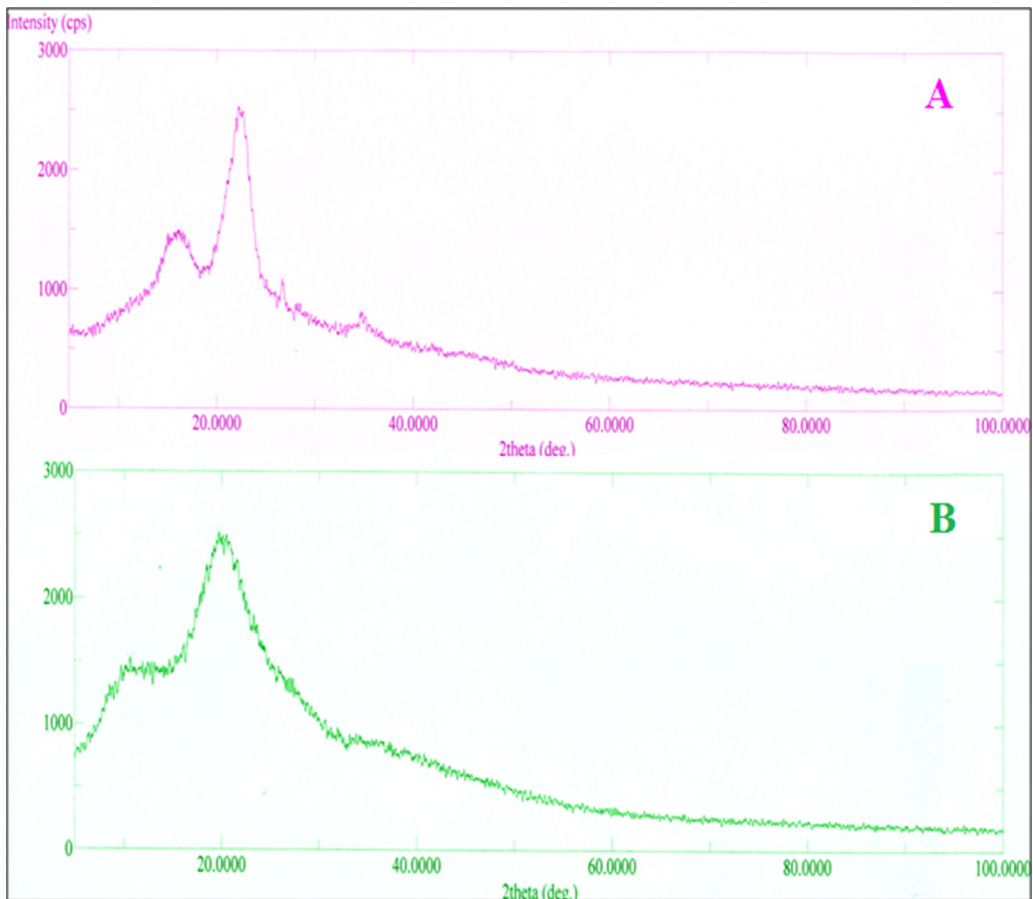**Fig. 4.** TGA and DSC curves of acetylated cellulose.

Fig. 5. The XRD patterns of (A) treated RH cellulose and (B) cellulose acetate.

highest rate of weight loss of RH cellulose occurred at 375 °C, while acetylated product happened at 420 °C, respectively. This clearly indicated that the thermal stability of the acetylated cellulose is higher than that of native cellulose.

The measurement of the extent of disruption of the hydrogen bonds as well as quantify the heat energy was investigated by DSC (Biliaderis, Maurice, & Vose, 1980; Fringant, Desbrieres, & Rinaudo, 1996). It is also observed from Fig. 5, that the heat release from the compounds represents by the exothermic peaks at a maximum temperature of 346 °C for RH cellulose and 369 °C acetylated cellulose due to the disintegration of intramolecular interaction and the decomposing of the polymer (Sun et al., 2004).

The RH cellulose show four diffraction peaks at $2\theta = 14.9°$, 16.1°, 22.2° and 34.8° characteristic of cellulose crystal I. These signals were assigned to the diffraction planes 101, 101, 002, and 040, respectively (Matsumura, Sugiyama, & Glasser, 2000). A shoulder peak at 16.1° and a weak peak at 34.8° indicate the removal of lignin and hemicellulose from the RH (Guozhi et al., 2013). The weak diffraction peaks appear around 10.6° in the diffraction pattern of cellulose acetate, attributed to the crystalline peaks of cellulose acetate II (Deus, Friebolin, & Siefert, 1991). In addition, the new diffraction peak at around $2\theta = 19.7°$, which was commonly assigned to the less ordered or amorphous region of the cellulose chains (Freire, Silvestre, Pascoal Neto, Belgacem, & Gandini, 2006). The acetylated cellulose display a low degree of crystallinity compared with that of the original cellulose which is resulted by the fact that the substitution of the hydroxyl groups by acetyl groups with greater volume, which broke the inter- and intra-molecular hydrogen bonds of cellulose (Hu, Chen, Xu, & Wang, 2011).

4. Conclusions

The isolation of cellulose from rice husk (RH) by an effective three-step processes like de-wax by 2:1 (v/v) hexane/methanol extraction, alkaline and acid treatments for the removal of lignin and hemicelluloses, respectively. After that cellulose was treated with hydrogen peroxide for whitening the colour. In presence of Lewis acid catalyst (iodine), cellulose was successfully esterified under solvent-free conditions. The degree of substitution, functional group and chemical structure of cellulose acetate were characterized with the help of FT-IR, ^{1}H NMR, XRD with the results of yield 66%. Moreover the thermal stability of the synthesized products was evaluated by TGA and DSC thermograms. The results showed that the overall degree of substitution increased as the amount of iodine increased and the cellulose acetate is thermally more stable than the native cellulose. Thus, the successful preparation of cellulose acetate would provide a promising opportunity to select the agricultural residues as a potent and competitive candidate for industrial utilization.

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